LOSS OF SPECTRAL CONTRAST IN HYPERFINE PALAGONITE: IMPLICATIONS FOR SMECTITE ON MARS.

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Smectite clays have long been regarded as good candidates for the silicate component of the fine-grained Martian dust. They have been observed in the SNC meteorites [1], have been predicted as the alteration product of silicate glass based on thermodynamics [2], are common in palagonite [3], and match the elemental composition of the soil measured at the Viking lander sites [4]. In terms of reflectance spectroscopy, iron-substituted smectite clays provide a good match to telescopic spectra of Mars [5,6], but Martian spectra lack a key feature that is characteristic of smectites, the 2.2 µm absorption due to a combination of stretching and bending of structural OH and metal-OH bonds.

Recent Earth-based spectra [7] and spectra from the ISM NIR imaging spectrometer on the Russian *Phobos 2* spacecraft [8] are reported to show a weak absorption feature around 2.2 µm. However, Dalton and Clark [9] report that the strength of this feature corresponds to not more than 0.5-1.0 wt% clay on the surface of Mars based on laboratory mixing studies. This abundance is clearly less than the 20-80% predicted to be present on the basis of thermodynamics and the chemistry of Martian soil [10].

Several explanations for the lack of the 2.2 µm feature in spectra of Mars have been proposed. First, many researchers believe that the dust is simply not smectite clay and prefer the analog palagonite [11,12], an amorphous weathering product of basaltic glass that has a similar chemical composition to smectite clay. However, the visible-NIR spectra of typical palagonite analogs have well developed water and 2.2 µm features due to the presence of smectite clays [13,3]. Alternatively, a variety of methods of suppressing the 2.2 µm absorption in soils with abundant smectite have been proposed. Oxidized clays have O^{2-} substituted for OH^- and exhibit weakened structural OH absorptions [14]. Mixtures of smectite clays with ferrihydrite or carbon black [6] also exhibit diminished spectral contrast. However, such physical mixtures fail to simultaneously match the albedo and spectral contrast observed in Mars spectra across all wavelenghths.

A simpler explanation for the lack of observed OH features in the Martian spectra that has not been fully examined is the role of particle size. Particle size plays a dominant role in determining albedo and spectral contrast of all materials, and additional effects are observed for extremely fine particles [15]. The dust particles on Mars are known to be less than a few microns is diameter [16]. We thus present here preliminary analyses of reflectance spectra of naturally produced fine grained particles which exhibit very weak 2.2 µm features.

Experimental Methods. The preparation of very fine particle size separates through grinding and sieving may not adequately parallel natural processes for the production of fine grained particles because mechanical grinding mixes materials of a variety of crystalline

scale lengths while the natural production of fine particles may preferentially produce particles with short-range order. We used a palagonitic soil from Haleakala, Hawaii (sample HK-3b). The original sample contained unaltered basaltic glass as well as palagonitized material. Passing this material through a 250 mm sieve removed most of the unaltered material.

The altered material was sifted into the following particle size series: 250-150, 150-75, 75-45, 45-25, 25-10, 10-5 and <5 µm. Microscopic observations of samples of each fraction under reflected light showed that there were relatively few clinging fines, so samples were not washed. However, the 10-5 µm sample was wet sieved with ethanol to obtain a sufficient quantity of <5 µm particles for reflectance measurements.

Reflectance spectra from each sample were obtained in a Nicolet FTIR spectrometer over the wavelength range from 0.9-26.0 µm relative to a diffuse gold standard. The atmosphere in the Nicolet was purged of H_2O and CO_2 with N_2. In the NIR region, the reflectance spectra match the spectral character of smectite clays with a well developed metal-OH absorption at 2.2 µm, water absorptions at 1.9 and longwards of 2.3 µm, and a combination overtone at 1.4 µm.

Results. Figure 1 shows the reflectance spectrum of each particle size separate from 1.2 to 2.6 µm. Each spectrum has been scaled to unity at 2.107 µm and offset by 5% for ease of comparison of the relative band strengths. One-sided band strengths were calculated for the absorptions at 1.4 and 2.2 µm, and a two sided band strength was calculated for the 1.9 µm band [17]. Figure 2a illustrates the effect of particle diameter (D) on these band strengths, especially in the small particle size regime (D <50 mm). Particle diameters are simply the median value of the distribution derived from sieving and thus exhibit some uncertainty. However, detailed particle size measurements of separates prepared with the same sieves and methods showed the median value corresponds well with the actual particle size [15]. In general, the band strengths behave as expected from theoretical considerations of particle size which predict a maximum band strength at a mean particle diameter equal to the inverse of the absorption coefficient at the band center and band strengths approaching 0 with decreasing particle size [18].

The decrease in band strength for the four smallest particle sizes below the maximum band strength can be approximated by a logarithmic function of particle diameter (Figure 2b). Extrapolation of a least squares fits of these data points allows a first order estimate of band strength for smaller particle sizes. The effective particle diameter for dust on Mars is   2.5-3.5 mm [16], although smaller values (<0.8 mm) have been proposed [19] and smaller particles may be more abundant [20]. For the 2.2 mm feature, band strength decreases from 2.2% at D=2.5 mm to <1% for D<0.6 mm. Mixing of this material with others would reduce the spectral

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contrast even further. Thus a simple explanation for the apparent lack of absorption features due to smectite clays is that the weathering products on Mars are so fine grained that the diagnostic 2.2 µm absorption is not detected.

The weathering process on Mars as on Earth is capable of producing extremely fine particles.   On Earth, these are typically removed by the action of water and sequestered in sedimentary reservoirs.   On Mars, however, they remain in the surface environment as dust. Since these fine particles are produced by in situ processes, it is important for Mars spectral analog studies to examine the effects of naturally produced hyperfine particles on reflectance spectra.   Hyperfine particles produced through mechanical grinding of bulk samples or soils may not adequately create particles with short-range crystalline order. Further work will examine the differences between naturally and mechanically produced fines. In addition, a more detailed characterization of the mineralogy and particle size of these samples is also planned.

Conclusions. Decreasing particle size in a palagonitized soil results in reduced spectral contrast in key reflectance features that are used for determining Martian mineralogy. While these samples do exhibit characteristic smectite clay features, the absorptions are weak and decrease in strength as particle size decreases. For the 2.2 µm feature, the strongest absorption is 4% for particle diameters of   75 µm and decreases to 2% at a diameter of   2.5 µm. Similar behavior is observed for the 1.4 and 1.9 µm bands. We thus conclude that the absence of a strong 2.2 mm absorption in the spectra of Mars does not preclude smectite clay as a key component for the Martian dust. Indeed, detection of smectites should be difficult given the small particles size of typical Martian dust.

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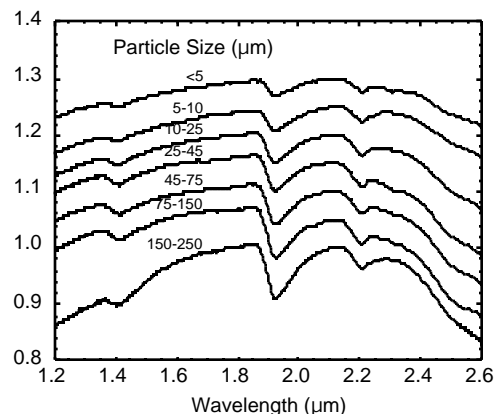

Figure 1. Scaled reflectance spectra of the particle size separates of sample HK-3b, a palagonitized soil from Hawaii. The three absorptions are due to H_2O and OH^- in the structure of smectite clay. The strength of each absorption decreases with particle size. Each spectrum is scaled to unity at 2.107 mm and offset by 5% for clarity.
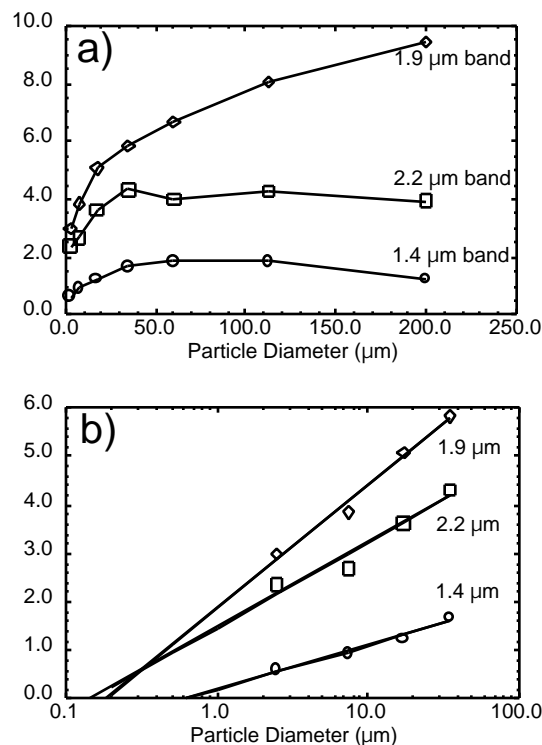

Figure 2. a) Band strength of the three principal absorptions as a function of particle size. **b)** Least squares logarithmic fit of the four smallest particle sizes. This fit is extrapolated to smaller particle sizes to provide a rough estimate of the behavior of the absorption bands at Martian particle sizes (D<2.5mm).